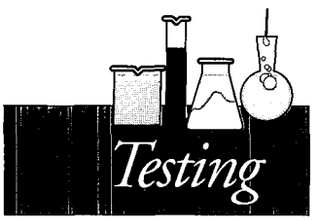


Novel methods for laboratory evaluation of deinking surfactants

John K. Borchardt, Pierre N. Tut

ABSTRACT: Two new laboratory methods for studying the process of ink separation from cellulose fibers are presented. A modified spinning-drop tensiometer can measure the interfacial tension between deinking surfactants and model inks within the time frame of the pulping stage. One-dimensional ^1H nuclear magnetic resonance imaging can measure the rate at which model inks separate from cellulose fibers. Both methods show promise as rapid screening tools for predicting the deinking effectiveness of deinking surfactants.

KEYWORDS: Cellulose fibers, deinking, development, evaluation, ink, nuclear magnetic resonance, reclaimed fibers, separation, scanning electron microscopy, surface tension, surfactants, test methods.

The laboratory methods used to study deinking are usually models of mill pulping, washing, flotation, thickening, and bleaching operations. Deinking effectiveness is evaluated on the basis of paper brightness and image analysis. While such tests are useful for studying the effects of deinking process variables, they provide little insight into the detailed nature of the physical and chemical events occurring during the two deinking process steps—ink detachment from fibers and dispersion during the pulping step followed by separation of the dispersed ink from the cellulose fibers. This report illustrates the application of modern laboratory instruments to obtain information on the mechanism of ink detachment from cellulose fibers.

Test methods and results

Dynamic interfacial tension

Experts in the field of deinking have observed that "deinking is fundamentally a laundering process" *(1, 2)*. Interfacial tensiometry has been used extensively in laundering (detergency) studies *(3, 4)*. Therefore, it seemed reasonable to investigate application of interfacial tensiometry to the study of deinking.

Interfacial tension (IFT) and surface tension are measured using a spinning-drop tensiometer (SDT). IFT values are based on the dimensions of oil-phase droplets, while surface tension values are determined from the dimensions of air bubbles. Analysis involves measuring the length of air bubbles or the length and width of oil-phase droplets or air bubbles.

The process time for deinking or for deresination of wood pulp is usually shorter than the time required for the IFT to reach equilibrium. If the IFT measurements are to be useful, they must be obtained within the time frame of the appropriate deinking process, i.e., while the IFT is still changing. Measurement of droplet dimensions using a conventional SDT requires a great deal of time. Consequently, conventional measurements of IFT at the short elapsed contact times typical of deinking processes are difficult and imprecise.

Two University of Texas Model 500 SDTs were modified by the addition of highly light-sensitive cameras and video equipment interfaced with a microcomputer containing a video board and image-analysis software. **Figure 1** is a schematic diagram of the configuration for the apparatus. The design of the apparatus is detailed in the literature *(5)*.

Using this apparatus, equilibrium IFT values can be determined with greater accuracy and in less time than with the manual method *(5)*. Dynamic IFT values, which are determined before the IFT value reaches equilibrium, can be measured accurately at intervals as short as 1 s. Images can be analyzed immediately or recorded on videotape for later study.

A study of dynamic IFT was performed to examine the effect of pH on IFT between surfactant solutions and a model of letterpress ink. The oil

Borchardt, research manager, pulp & paper surfactants, Tutunjian, senior research chemist, and Prieto, research chemist, are affiliated with Shell Chemical Co., Westhollow Research Center, P.O. Box 1380, Houston, TX 77251-1380.

Novel methods for laboratory evaluation of deinking surfactants

John K. Borchardt, Pierre N. Tutunjian, and Nelson E. Prieto

ABSTRACT: Two new laboratory methods for studying the process of ink separation from cellulose fibers are presented. A modified spinning-drop tensiometer can measure the interfacial tension between deinking surfactants and model inks within the time frame of the pulping stage. One-dimensional ^1H nuclear magnetic resonance imaging can measure the rate at which model inks separate from cellulose fibers. Both methods show promise as rapid screening tools for predicting the deinking effectiveness of deinking surfactants.

KEYWORDS: Cellulose fibers, deinking, development, evaluation, ink, nuclear magnetic resonance, reclaimed fibers, separation, scanning electron microscopy, surface tension, surfactants, test methods.

The laboratory methods used to study deinking are usually models of mill pulping, washing, flotation, thickening, and bleaching operations. Deinking effectiveness is evaluated on the basis of paper brightness and image analysis. While such tests are useful for studying the effects of deinking process variables, they provide little insight into the detailed nature of the physical and chemical events occurring during the two deinking process steps—ink detachment from fibers and dispersion during the pulping step followed by separation of the dispersed ink from the cellulose fibers. This report illustrates the application of modern laboratory instruments to obtain information on the mechanism of ink detachment from cellulose fibers.

Test methods and results

Dynamic interfacial tension

Experts in the field of deinking have observed that "deinking is fundamentally a laundering process" *(1, 2)*. Interfacial tensiometry has been used extensively in laundering (detergency) studies *(3, 4)*. Therefore, it seemed reasonable to investigate application of interfacial tensiometry to the study of deinking.

Interfacial tension (IFT) and surface tension are measured using a spinning-drop tensiometer (SDT). IFT values are based on the dimensions of oil-phase droplets, while surface tension values are determined from the dimensions of air bubbles. Analysis involves measuring the length of air bubbles or the length and width of oil-phase droplets or air bubbles.

The process time for deinking or for deresination of wood pulp is usually shorter than the time required for the IFT to reach equilibrium. If the IFT measurements are to be useful, they must be obtained within the time frame of the appropriate deinking process, i.e., while the IFT is still changing. Measurement of droplet dimensions using a conventional SDT requires a great deal of time. Consequently, conventional measurements of IFT at the short elapsed contact times typical of deinking processes are difficult and imprecise.

Two University of Texas Model 500 SDTs were modified by the addition of highly light-sensitive cameras and video equipment interfaced with a microcomputer containing a video board and image-analysis software. **Figure 1** is a schematic diagram of the configuration for the apparatus. The design of the apparatus is detailed in the literature *(5)*.

Using this apparatus, equilibrium IFT values can be determined with greater accuracy and in less time than with the manual method *(5)*. Dynamic IFT values, which are determined before the IFT value reaches equilibrium, can be measured accurately at intervals as short as 1 s. Images can be analyzed immediately or recorded on videotape for later study.

A study of dynamic IFT was performed to examine the effect of pH on IFT between surfactant solutions and a model of letterpress ink. The oil

Borchardt, research manager, pulp & paper surfactants, Tutunjian, senior research chemist, and Prieto, research chemist, are affiliated with Shell Chemical Co., Westhollow Research Center, P.O. Box 1380, Houston, TX 77251-1380.

phase of the model ink was 90% mineral oil and 10% methyl oleate. A typical letterpress ink composition is 70–90% mineral oil, 0–15% binder resin, 10–15% carbon black, plus small amounts of other additives such as waxes. The methyl oleate was added to model the more polar additives in letterpress inks. The test surfactant was AE 1415-7, an alcohol ethoxylate containing 14–15 carbons in the surfactant hydrophobe and seven ethoxy groups. Neither the test conditions nor the test surfactant were optimized to minimize IFT.

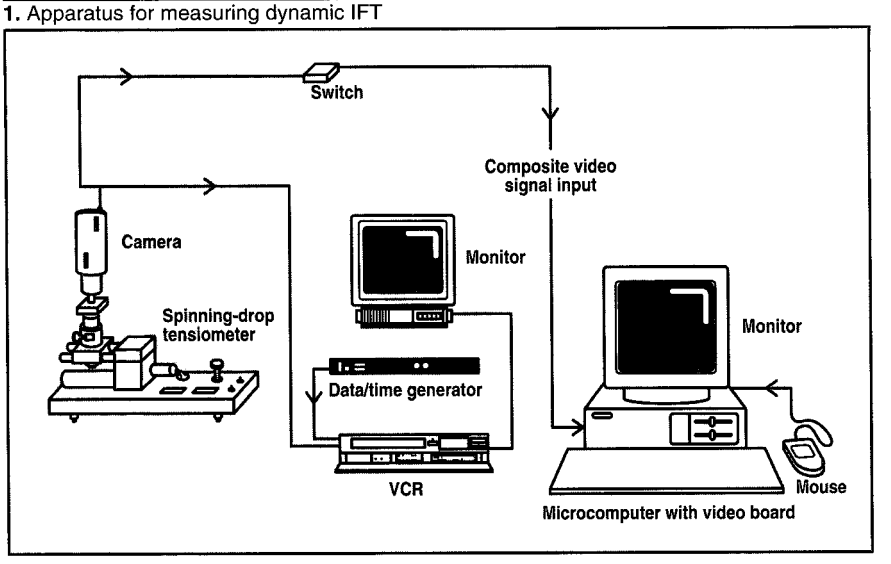
The results in **Fig. 2** show the effect of pH on IFT between surfactant AE 1415-7 and the model ink. For typical pulping and flotation times of 5–30 min, differences in dynamic IFT values at pH 9 and pH 5.5 were only 1–2 dynes/cm. This would lead one to predict little difference in deinking efficiency at these pH values.

Flotation deinking studies

This prediction was tested by conducting flotation deinking experiments under the same conditions as the dynamic IFT measurements. Flotation deinking experiments were performed at pH 9.0 and pH 5.5 *(6)*. Results are summarized in **Table I**. The test surfactant (AE 1415-7) was the same as used in the dynamic IFT experiments. Two letterpress furnishes, the *Atlanta Journal and Constitution* and *The Houston Post*, were chosen for these experiments. Again, neither the deinking process conditions nor the surfactant were optimized to minimize IFT.

Consistent deinking results were obtained for both newsprints. Generally, handsheet brightness was slightly greater at pH 5.5 than at pH 9.0. Fiber loss in the acidic media also appeared to be lower than that observed at pH 9.0. Consistent deinking results also were obtained using AE 1415-13 at pH 5.5 and pH 9.0.

1. Apparatus for measuring dynamic IFT



Laboratory results for flotation deinking were surprisingly consistent with the results of the dynamic IFT experiment, even though foaming plays no role in the dynamic IFT experiment.

One-dimensional NMR imaging

The optical opacity of pulp slurries prevents the use of traditional light microscopy in the study of ink removal from cellulose fibers. Hydrogen (^{1}H) nuclear magnetic resonance (NMR) imaging techniques have been developed in our laboratory for a variety of analyses. (Medical applications of three-dimensional NMR imaging are well known.) The use of ^{1}H NMR imaging to study the removal of oil phases from fibers and its application to deinking is described in the following paragraphs.

The test setup is illustrated in **Fig. 3**. Fiber samples were epoxied to the bottom of a test tube and then saturated with dodecane. Paper (an unprinted newsprint consisting of 100% virgin pulp), cotton, and a 1:1 polyester/cotton blend were the fibers chosen for study. Dodecane was chosen as the contaminant because it is a reasonable model of the mineral-oil vehicles used in letterpress inks. Dodecane also has been used as a model of nonpolar soils removed in laundering.

The sample tube was inserted into the NMR spectrometer probe immediately after addition of 15 cm^3 of deuterium oxide (heavy water) and surfactant AE 12-4 (0.5% by weight). The use of deuterium oxide as a solvent instead of water eliminates most of the water protons as a source of NMR signals. The largest NMR signal is due to the hydrogen atoms in the dodecane. Further details about the experimental design are provided in the literature *(6)*.

Surfactant AE 12-4 is a linear 12-carbon alcohol ethoxylate with four ethoxy groups. The surfactant promotes migration of the dodecane from the fiber into the aqueous phase in the x-direction. This migration is studied as a function of time via x-direction profiling.

Figure 4 is a plot of the x-direction profiles over time for a dodecane-saturated 1:1 polyester/cotton disk. The large peak in the center of the spectrum at 5.7 min represents the one-dimensional x-direction profile of the dodecane distribution in the fiber disk. The smaller signal that extends on ei-

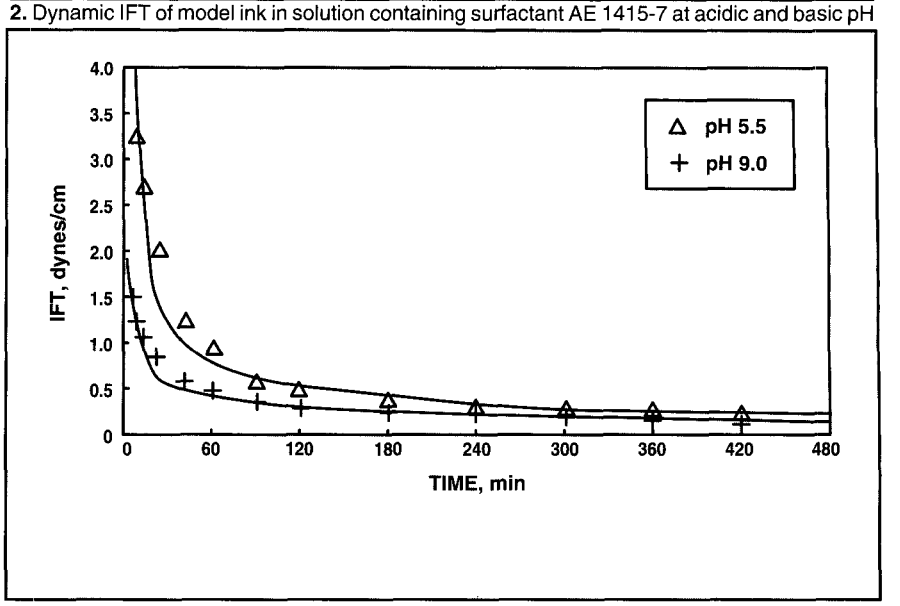
ther side of the major peak represents the one-dimensional x-direction profile of the dodecane that has been removed from the fiber disk by the surfactant and is now distributed in the aqueous phase, i.e., across the whole width of the vial. The peaks at either end of the profile are due to the meniscus effect at the liquid–air–glass interface, as seen in Fig. 3.

The x-direction profiles of Fig. 4 indicate a steady decrease in signal from dodecane in the fiber disk with a simultaneous increase in the signal from the dodecane distributed across the vial in the aqueous phase. This indicates that the dodecane was removed from the fiber disk, with the emulsified dodecane then being distributed across the diameter of the vial. Profiles along the vertical y-direction [Borchardt *et al. (6)*] indicate that the dodecane from the disk did not distribute itself evenly through the liquid above the disk. Instead, it formed a thin layer at the surface of the aqueous phase.

The relative concentration of dodecane remaining in the fibers upon exposure to a surfactant solution was determined as a function of time. (The experimental measure of dodecane concentration was the integrated signal intensity of the ^{1}H NMR peak caused by the dodecane in the fiber disk.) Without surfactant, there was no significant removal of dodecane from either paper or the 1:1 polyester/cotton blend *(6)*. In contrast, there was a rapid decrease in the dodecane content of the cotton fabric. After this initial decrease, there was no detectable further loss of dodecane from the cotton.

Figure 5 shows the results for the three materials in the presence of surfactant AE 12-4 and illustrates the usefulness of the method. [For additional results, see Borchardt *et al. (6)*.] Dodecane removal from both cotton and polyester/cotton was observed. Removal of dodecane from paper was substantially slower than dodecane removal from the two fabrics. After 30–50 min, more than 80% of the dodecane was removed from the fabrics, while there was no significant dodecane removal from paper.

2. Dynamic IFT of model ink in solution containing surfactant AE 1415-7 at acidic and basic pH



Discussion

Deinking experts have observed similarity between the processes of wash deinking and laundering clothes *(1, 2)*. Laundering, often termed detergency, has been studied extensively *(7)*. With a better understanding of the similarities and differences between removal of ink particles from cellulose and cloth fibers, it should be possible to determine the extent to which the extensive detergency literature can be used to understand the deinking process.

Dynamic IFT and deinking studies

Dynamic IFT measurements and deinking tests were each performed at two different pH values. Results from both tests were consistent. In other words, the much faster dynamic IFT measurements predicted the relative results obtained in the lengthy deinking experiments. Thus dynamic IFT appears to be a useful rapid screening tool for evaluating (a) the deinking effectiveness of a surfactant or (b) the effect of different pulping conditions on ink removal.

The results of deinking experiments performed at pH 5.5 during both pulping and flotation (Table I) imply that pulping pH of newsprint might be reduced without an adverse effect on deinking effectiveness. Additional studies using a better model of mill pulping are probably required to verify this tentative conclusion.

One-dimensional NMR imaging studies

An initially rapid loss of dodecane from cotton fiber was observed repeatedly in one-dimensional NMR imaging experiments. This was true even in the absence of surfactant. Much of the dodecane was removed from cotton in the first few seconds of an experiment before an accurate NMR signal could be obtained. This suggests that dodecane's affinity for cotton is relatively small.

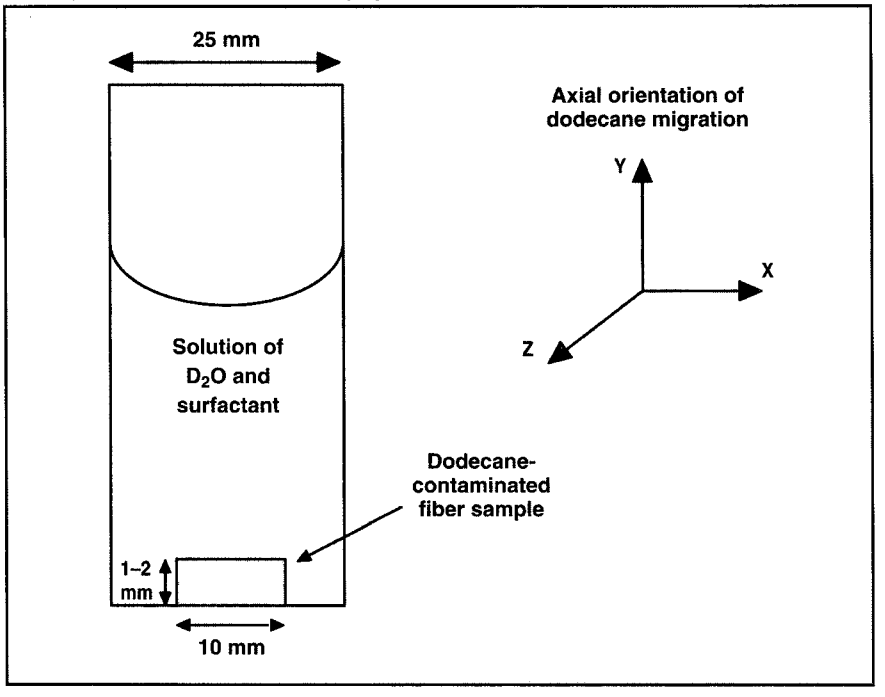
Microscopy studies *(6)* suggest that the different morphologies of paper and fabrics of cotton or cotton/polyester can account for the much slower rate of dodecane removal from paper than from the fabrics. In fabric, individual fibers are twisted together and then woven. Much of the soil removed in laundering (and much of the dodecane in the NMR imaging experiments) is lodged in the large gaps between fibers. Paper contains no such large gaps. [See Figs. 14 and 15 in Borchardt *et al. (6)*.] In paper, ink (and the dodecane used in the NMR imag-

I. Effect of pH on flotation deinking[a]

Deinking surfactant	Furnish[b]	pH[c]	Flotation deinking: Brightness, %	Flotation deinking: Image analysis particle area, ppm	Flotation deinking: Fiber loss, %
AE 1415-7	AJC	9.0	55	...	...
		5.5	58	86	6.0
	HP	9.0	47	81	8.6
		5.5	52	106	7.8
None	HP	9.0	52[d]	...	0.01
		9.0	40	...	1.0
		9.0	42	82	2.0
AE 1415-13	AJC	9.0	55	...	...
		5.5	58	94	7.9
	HP	9.0	49	138	7.6
		9.0	51	...	12.2
		5.5	51	150	16.6

[a]Temperature = 110°F. Surfactant concentration was 0.2% by weight relative to old newspaper.
[b]HP = *The Houston Post*; AJC = *Atlanta Journal and Constitution.*
[c]The pH for the pulping and flotation stages was identical.
[d]Unprinted paper cut from the edges of the newspaper. Brightness of this material can be considered to be the maximum possible in the absence of a bleaching stage.

3. Sample tube used in ^1H NMR imaging experiments



ing experiments) is located in the much smaller gaps between fibers as well as on fiber surfaces. Removal of dodecane films from fiber surfaces may be similar for the three types of fibers. (The very rapid initial loss of dodecane from cotton may be an exception to this generalization.) However, the surfactant solution more easily penetrates large gaps between fibers than small ones. Thus the surfactant solution more rapidly contacts the dodecane in fabrics than in paper.

The rate of dodecane removal from paper was initially more rapid using surfactant AE 1215-9 instead of AE 12-4 *(6)*. As seen in Fig. 5, dodecane removal in the presence of AE 12-4 became appreciable only after about 500 min. The dodecane declined to about 70% of its initial value after 20 h. In the presence of the more-polar AE 1215-9, dodecane content in the paper declined to about 70% of the initial value after only 2 h, with little further dodecane removal in the next 20 h of the experiment.

These imaging results are consistent with the known effects of surfactant polarity on wash deinking effectiveness. Turai and Williams *(8)* have reported that paper brightness after wash deinking increased with increasing surfactant polarity to a maximum at an HLB (hydrophilic:lipophilic balance) value of 14–15. The HLB value of AE 1215-9 is 13.3. The HLB values of AE 12-3 and AE 12-4 are substantially lower at 9.6 and 11.0, respectively.

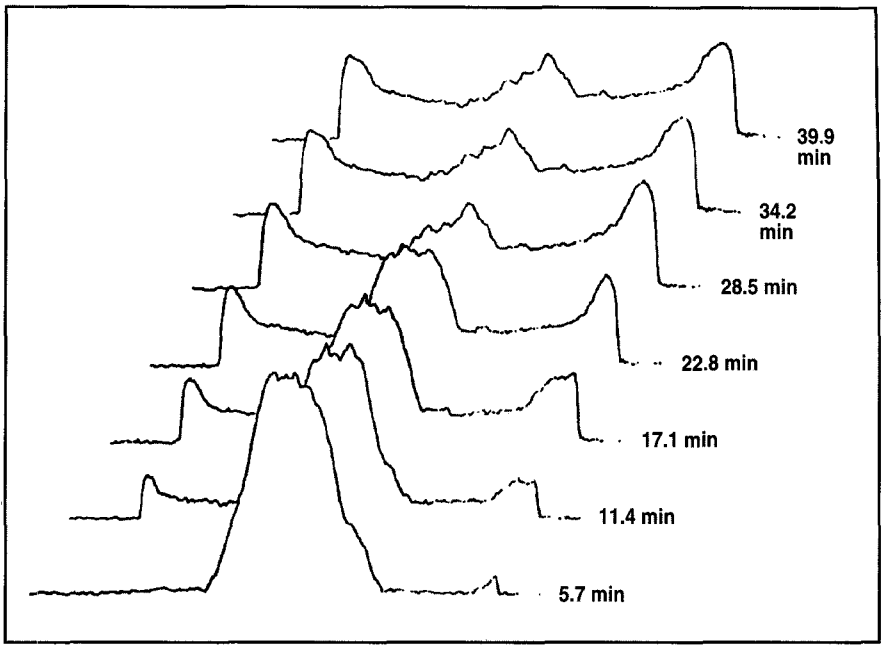
One-dimensional NMR imaging provides information on the relative kinetics of model ink removal within 2.5 h. (Preparation of a single sample requires less than 30 min.) The experiment is automated during most of the measurement time, allowing the operator to work on other tasks. In contrast, a wash-deinking experiment takes 2–3 h of continuous work on the part of the operator.

The contact time between fiber and surfactant solution is much greater in the NMR experiment than in deinking. (A typical pulping time is 30–45 min.) However, the mechanical mixing during pulping provides more effective contact of the surfactant solution with the cellulose fibers. This efficient contact is not present during the NMR experiment. Therefore, the extended paper–surfactant solution contact time during NMR experiments is not unreasonable.

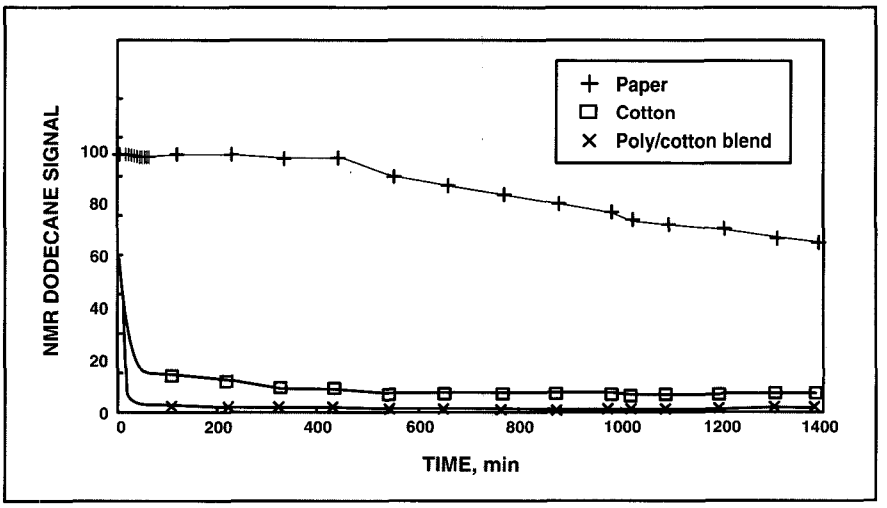
Literature cited

1. Woodward, T. W., 1991 Chemical Processing Aids Short Course, TAPPI PRESS, Atlanta, p. 85.
2. Horacek, R. G., 1989 Contaminant Problems and Strategies in Wastepaper Recycling Seminar, TAPPI PRESS, Atlanta, p. 45.
3. Raney, K., J. Amer. Oil Chem. Soc. 68: 525(1991).
4. Curie, P. K. and van Nieuwkoop, J., J. Colloid and Interface Sci. 87: 301(1982).
5. Borchardt, J. K., and Yates, C.W., J. Am. Oil Chem. Soc. 70:47(1993).
6. Borchardt, J. K., Tutunjian, P. N., Rask, J.

4. Time sequence of one-dimensional ^1H NMR signals observed in sample tube containing dodecane-saturated disk of cotton/polyester fibers in a solution of surfactant and heavy water. The central peak represents the initial quantity of dodecane in the fiber disk. The peaks at the edges depict the increasing quantity of dodecane dispersed in the aqueous phase and reflect the meniscus effect at circumference of the tube.



5. Results of one-dimensional ^1H NMR imaging experiment showing dodecane removal from fibers in a solution of heavy water and surfactant AE 12-4 (0.5% by weight)



H., *et al.*, 1992 Contaminant Problems and Strategies in Wastepaper Recycling Seminar, TAPPI PRESS, Atlanta, p. 85.
7. Cutler, W. G. and Kissa, E., Detergency: Theory and Technology, Vol. 20, Surfactant Science Series, Marcel Dekker, New York, 1987.
8. Turai, L. L. and Williams, L. D., Tappi 60(11): 167(1977).

Received for review July 2, 1992.

Accepted Nov. 10, 1992.

Presented at the TAPPI 1992 Contaminant Problems and Strategies in Wastepaper Recycling Seminar.